2636 *Inorg. Chem.* **2001,** *40,* 2636−2637

Synthesis and Reactivity of Fluoro Complexes. Part 1. Cyclooctadiene Rhodium(I) Complexes

José Vicente,*,† Juan Gil-Rubio,† and Delia Bautista‡

Grupo de Química Organometálica, Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, Apartado 4021, Murcia, 30071 Spain, and SACE, Universidad de Murcia, Apartado 4021, Murcia, 30071 Spain

Received March 22, 2001

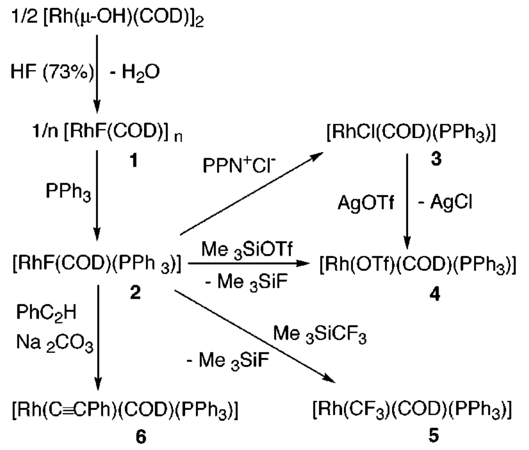
There is a growing interest in the study of transition metal organometallic fluoro complexes.[1] The unique properties of fluorine impart an unusual reactivity to the metal−fluorine bond which can be exploited in preparative organometallic chemistry[2] or in catalysis.[3] In addition, the development of transition metal mediated C−F bond formation processes is still a virtually unexplored field.[4]

The number of rhodium(I) fluoro complexes is still scarce, and very few studies on their reactivity have been reported.[5] To the best of our knowledge, only two Rh(I) fluoro complexes without phosphine, arsine, or stibine ligands have been prepared. The first, temptatively formulated as $[Rh(\mu\text{-}F)(cyclooctene)_2]_2$, was obtained by reacting $[Rh(\mu\text{-}Cl)(cyclooctene)_2]_2$ with AgF.[5c] The second was the tetramer $[Rh(\mu^3\text{-}F)(C_2H_4)(C_2F_4)]_4$, which was prepared by the successive treatment of $[Rh(\mu\text{-}Cl)(C_2H_4)(C_2F_4)]_2$ with $AgBF_4$ and the fluoride donor reagent $[(Me_2N)_3S]^+[Me_3SiF_2]^-$.[5f]

Herein, we report the synthesis of two novel rhodium(I) fluoro complexes containing cyclooctadiene (COD) and a preliminary study of the reactivity of the Rh−F bond, which is shown to be substantially different from that of the other Rh−halogen bonds.

Treatment of $[Rh(\mu\text{-}OH)(COD)]_2$[6] with 73% hydrofluoric acid in THF gave compound **1** as a yellow microcristalline precipitate in 82% yield (Scheme 1). The NMR spectra of **1** were of poor quality because, in contrast to $[Rh(\mu\text{-}X)(COD)]_2$ (X = Cl, OH), it is only sparingly soluble in organic solvents, which impeded determination of its structure in solution.[7] We were unable to grow single crystals of **1** for X-ray structure determination, however, we are currently attempting the preparation of more soluble fluoro complexes containing different dienes for its structural characterization.

Scheme 1



The main product of the reaction of compound **1** with 1 equiv of triphenylphosphine in THF is **2**, which was isolated in 59% yield. The crystal structure of **2** was determined by X-ray diffraction analysis[8] and shows a distorted square-planar coordination geometry (Figure 1). As expected from the greater trans influence of PPh_3 with respect to F^-, the Rh−C(5) and Rh−C(6) distances are longer than the Rh−C(1) and Rh−C(2) ones (Figure 1).

In the ^{19}F NMR spectrum of **2**, a broad singlet was observed at high field (δ −256.9 ppm in d_8-toluene) characteristic of Rh(I)-bound fluorine.[5j] The room temperature $^{31}P\{^1H\}$ NMR spectrum displays a broad singlet at at δ 23.0 ppm which splits into a broad doublet at $T < -20$ °C with $^1J_{RhP} = 159.3$ Hz.[9] The $^{31}P-^{19}F$ and $^{103}Rh-^{19}F$ couplings were not resolved even at −90 °C. This suggests that, although **2** is the main species present in solution, fast Rh−F and Rh−P bond dissociations take place to give products whose nature is still not clear. Complex **2** is the first fluoro complex of Rh(I) with only one phosphine ligand.

---

* To whom communication should be addressed.

† Grupo de Química Organometálica, Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia.

‡ SACE, Universidad de Murcia.

(1) (a) Doherty, N. M.; Hoffman, N. W. *Chem. Rev.* **1991**, *91*, 553−573. (b) Murphy, E. F.; Murugavel, R.; Roesky, H. W. *Chem. Rev.* **1997**, *97*, 3425−3468.

(2) (a) Veltheer, J. E.; Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 12478−12488. (b) Grushin, V. V. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 994−996. (c) Archibald, S. J.; Braun, T.; Gaunt, J. A.; Hobson, J. E.; Perutz, R. N. *J. Chem. Soc., Dalton Trans.* **2000**, 2013−2018.

(3) Pagenkopf, B. L.; Carreira, E. M. *Chem. Eur. J.* **1999**, *5*, 3437−3442.

(4) Barthazy, P.; Stoop, R. M.; Wörle, M.; Togni, A.; Mezzetti, A. *Organometallics* **2000**, *19*, 2844−2852.

(5) (a) Grinberg, A. A.; Singkh, M. M.; Varshavskii, Yu. S. *Russ. J. Inorg. Chem.* **1968**, *13*, 1399−1401. (b) Vaska, L.; Peone, J., Jr. *J. Chem. Soc., Chem. Commun.* **1971**, 418−419. (c) van Gaal, H. L. M.; van den Bekerom, F. L. A.; Verlaan, J. P. J. *J. Organomet. Chem.* **1976**, *114*, C35−C37. (d) van Gaal, H. L. M.; van den Bekerom, F. L. A. *J. Organomet. Chem.* **1977**, *134*, 237−248. (e) Goswami, K.; Singh, M. M. *J. Indian Chem. Soc.* **1979**, *56*, 477−482. (f) Burch, R. R.; Harlow, R. L.; Ittel, S. D. *Organometallics*, **1987**, *6*, 982−987. (g) Araghizadeh, F.; Branan, D. M.; Hoffman, N. W.; Jones, J. H.; McElroy, E. A.; Miller, N. C.; Ramage, D. L.; Battaglia Salazar, A.; Young, S. H. *Inorg. Chem.* **1988**, *27*, 3752−3755. (h) Fryzuk, M. D.; Piers, W. E. *Polyhedron* **1988**, *7*, 1001−1014. (i) Sakakura, T.; Sodeyama, T.; Sasaki, K.; Wada, K.; Tanaka, M. *J. Am. Chem. Soc.* **1990**, *112*, 7221−7229. (j) Gil-Rubio, J.; Weberndörfer, B.; Werner, H. *J. Chem. Soc., Dalton Trans.* **2000**, 1437−1444. (k) Gil-Rubio, J.; Weberndörfer, B.; Werner, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 786−789.

(6) Usón, R.; Oro, L. A.; Cabeza, J. A. *Inorg. Synth.* **1985**, *23*, 126−130.

(7) Broad signals assignable to the COD ligand were observed in the ^1H and $^{13}C\{^1H\}$ NMR spectra of **1** (d_8-THF) at room temperature. No signals were observed in the ^{19}F NMR spectrum (d_8-THF) in the +20 to −380 ppm range (relative to external $CFCl_3$) at temperatures from +60 to −80 °C.

(8) Crystal data for **3** were recorded on a Siemens P4 difractometer, $\lambda = 0.71073$ Å, $C_{26}H_{27}FPRh$ (492.36), monoclinic ($P2_1/c$) $a = 12.7652(7)$ Å, $b = 11.3795(7)$ Å, $c = 14.6419(8)$ Å, $\beta = 95.728(4)°$, $V = 2116.3(2)$ Å^3, $Z = 4$, $\rho_{calc} = 1.545$ Mg/m^3, $\mu = 0.901$ mm^{-1}, $F(000) = 1008$, $T = 173(2)$ K; θ range = 3.08−25.00, $-15 \leq h \leq 15$, $-13 \leq k \leq 1$, $-17 \leq l \leq 0$; reflect. collected, 3891; indep reflns, 3720 ($R_{int} = 0.0140$), abs corr ψ-scans, max and min transmission 0.79798 and 0.75555; structure refinement full-matrix least squares on F^2, data/restraints/parameters 3720/208/262, GOF on $F^2 = 1.057$, final R indices [$I > 2\sigma(I)$], R1 = 0.0205, all data wR2 = 0.0498; largest diff peak and hole 0.372 and −0.331 eÅ^{-3}.

(9) This value is similar to the ones found in $[RhCl(COD)(PR_3)]$ complexes; see Naaktgeboren, A. J.; Nolte, R. J. M.; Drenth, W. *J. Am. Chem. Soc.* **1980**, *102*, 3350−3354.

10.1021/ic015526e CCC: $20.00

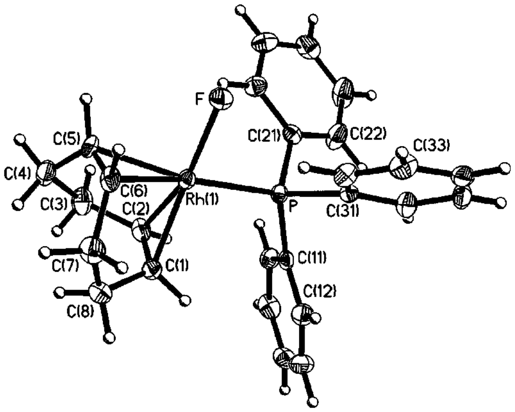


Figure 1. Molecular structure of **2** with 50% probability ellipsoids and the labeling scheme. Selected bond lengths (Å) and angles (deg): Rh−F 2.0214(12), Rh−C(1) 2.115(2), Rh−C(2) 2.097(2), Rh−C(5) 2.197(2), Rh−C(6) 2.189(2), C(1)−C(2) 1.399(3), C(5)−C(6) 1.379(3), Rh−P 2.3229(5); F−Rh−C(5) 89.06(7), F−Rh−C(6) 87.24(7), C(1)−Rh−P 96.92(6), C(2)−Rh−P 92.86(6), F−Rh−P 89.40(4).

Treatment of **2** with PPN^+Cl^- (PPN = $[Ph_3P]_2N$) gave quantitatively the chloro complex **3**.[10] The reaction of **2** with $Me_3SiO_3SCF_3$ afforded Me_3SiF, which was detected by ^1H and ^{19}F NMR spectroscopy, and compound **4** in 87% yield. The triflate **4** can be also prepared by the reaction of **3** with $AgCF_3SO_3$.

The reaction of **2** with Me_3SiCF_3 afforded complex **5**, which was isolated in 76% yield, and Me_3SiF. This synthethic method has been previously used only for the preparation of Ru and Os trifluoromethyl complexes.[11] We were interested in testing this method on Rh(I) fluoro complexes since only one Rh(I) trifluoromethyl complex is known.[12] The crystal structure of **5** was determined by X-ray diffraction (Figure 2).[13] Two independent molecules were found in the unit cell which show very small differences in both bond distances and angles. In contrast to complex **2**, the Rh−C distances were similar for both Rh−olefin bonds, which suggest that CF_3 and PPh_3 have similar trans influences. This is the first crystal structure determination of a Rh(I) trifluoromethyl complex. In C_6D_6 solution, the $^{31}P\{^1H\}$ NMR spectrum shows a doublet of quartets with $^1J_{RhP} = 177.9$ Hz and $^3J_{PF} = 21.4$ Hz.

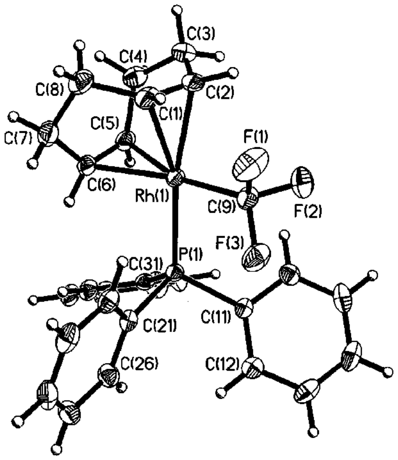


Figure 2. Molecular structure of **5** with 50% probability ellipsoids and the labeling scheme. Only one of the two independent molecules is displayed. Selected bond lengths (Å) and angles (deg): Rh(1)−C(9) 2.097(2), Rh(1)−C(1) 2.215(2), Rh(1)−C(2) 2.194(2), Rh(1)−C(5) 2.208(2), Rh(1)−C(6) 2.206(2), Rh(1)−P(1) 2.3245(5), C(1)−C(2) 1.381(3), C(5)−C(6) 1.379(3); C(9)−Rh(1)−C(2) 87.60(9), C(9)−Rh(1)−C(1) 91.55(8), C(9)−Rh(1)−P(1) 91.13(6), C(6)−Rh(1)−P(1) 90.01(6), C(5)−Rh(1)−P(1) 96.71(6).

The alkynyl complex [Rh(C≡CPh)(COD)(PPh_3)] (**6**) was obtained in 79% yield by reaction of **2** with 1 equiv of phenyl acetylene in the presence of Na_2CO_3, which neutralized the HF formed in the reaction.[5j] It is noteworthy that [RhCl(COD)(PPh_3)] does not react appreciably with phenyl acetylene under the same conditions. The presence of the alkynyl unit was confirmed by the IR [ν(C≡C) = 2084 cm^{-1}] and ^{13}C NMR spectra, which displayed two doublets at δ 121.5 ppm ($^1J_{RhC} = 48.6$ Hz) and 120.8 ppm ($^2J_{RhC} = 12.2$ Hz) for the α and β alkynyl carbons, respectively. An exchange process involving dissociation of the phosphine is likely responsible for the absence of the $^{13}C_{\alpha,\beta}-^{31}P$ couplings and for the broad singlet observed in the $^{31}P\{^1H\}$ NMR spectrum at room temperature. On cooling at −10 °C, this broad singlet was transformed into a doublet ($^1J_{RhP} = 159.8$ Hz).

Recently, it has been reported that complexes of the general composition [Rh(C≡CAr)(Nbd)(PR_3)] generated in situ are excellent initiators for the controlled living polymerization of phenylacetylenes.[14] However, in contrast to **6**, these species are too unstable to be isolated. Preliminary experiments show that polymerization of phenylacetylene takes place in the presence of catalytic amounts of **2** or **6**, both in the presence of Na_2CO_3, to give polyphenylacetylene in a nearly quantitative yield.

Acknowledgment. We thank the DGICYT (PB97-1047 and a research contract to J.G.R.) and the European Commission (Contract HPMF-CT1999-00116) for financial support.

Supporting Information Available: Synthetic procedures, spectral and analytical data for **1**−**6**, crystallographic files in CIF format for compounds **3** and **5**, and ORTEP plots of the two independent molecules of **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC015526E

---

(10) Chatt, J.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 4735−4741.

(11) Huang, D.; Koren, P. R.; Folting, K.; Davidson, E. R.; Caulton, K. G. *J. Am. Chem. Soc.* **2000**, *122*, 8916−8931.

(12) *Trans*-[Rh(CF_3)(CO)(PPh_3)$_2$] was prepared by reacting *trans*-[RhH(CO)(PPh_3)$_2$] with the toxic Hg(CF_3)$_2$; see Burrell, A. K.; Clark, G. R.; Jeffrey, J. G.; Rickard, C. E. F.; Roper, W. R. *J. Organomet. Chem.* **1990**, *388*, 391−408.

(13) Crystal data for **5** were recorded on a Siemens P4 difractometer, λ = 0.71073 Å. $C_{27}H_{27}F_3Rh$ (542.37), triclinic ($P-1$), a = 11.8239(5) Å, b = 13.0316(7) Å, c = 15.0851(9) Å, α = 92.237(5)°, β = 99.544(4)°, γ = 90.658(4)°, V = 2290.1(2) Å^3, Z = 4, ρ_{calc} 1.573 Mg/m^3, μ = 0.853 mm^{-1}, $F(000)$ = 1104, T = 173(2) K; θ range = 3.10−25.00, $-14 \le h \le 14$, $-15 \le k \le 15$, $-17 \le l \le 5$; reflns collected, 11116; indep reflns, 8040 (R_{int} = 0.0145), abs corr ψ-scans, max and min transmission 0.78749 and 0.75721; structure refinement full-matrix least squares on F^2, data/restraints/parameters 8040/508/577, GOF on F^2 = 1.066, final R indices [$I > 2\sigma(I)$], R1 = 0.0211, all data wR2 = 0.0520; largest diff peak and hole 0.318 and −0.313 eÅ^{-3}.

(14) (a) Kishimoto, Y.; Miyatake, T.; Ikariya, T.; Noyori, R. *Macromolecules* **1996**, *29*, 5054−5055. (b) Kishimoto, Y.; Eckerle, P.; Miyatake, T.; Kainosho, M.; Ono, A.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1999**, *121*, 12035−12044.